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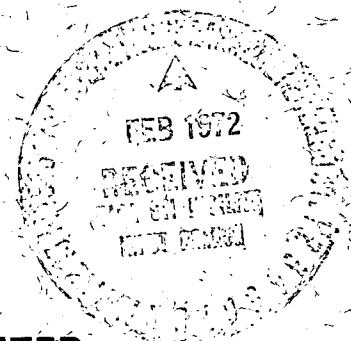
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# EARTH PHYSICS AND PHASE TRANSFORMATIONS PROGRAM: A Concept and Proposal

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**EARTH PHYSICS AND PHASE TRANSFORMATIONS PROGRAM:  
A CONCEPT AND PROPOSAL**

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"There are often great distances between the detailed laws and the main aspects of real phenomena. For example, if you watch a glacier from a distance, and see the big rocks falling into the sea, and the way the ice moves, and so forth, it is not really essential to remember that it is made out of little hexagonal ice crystals. Yet if understood well enough the motion of the glacier is in fact a consequence of the character of the hexagonal ice crystals. But it takes quite a while to understand all the behaviour of the glacier (in fact nobody knows enough about ice yet, no matter how much they've studied the crystal). However the hope is that if we do understand the ice crystal we shall ultimately understand the glacier."

—————Richard P. Feynman,

on 'The Character of Physical Law'

## ABSTRACT

A unique and far reaching program to study the geophysical characteristics of the planet earth is presented as an integration of the different disciplines that constitute the earth sciences, through the foundation of a generalized geodynamic theory of Earth Physics.

Every part of the physical system that constitutes the earth is a topic of vital interest to one or another scientific discipline. Thus, there are recognized topics such as seismology, geomagnetism, marine geomorphology, micropaleontology, and meteorology. Each of these disciplines has its challenging scientific problems of varying degrees of application to the concerns of society.

To understand such associated geophysical phenomena as weather and climate, volcanism, earthquakes, plate tectonics, and localization of mineral resources, the solutions of the formidable problems of the macroscopic hydrodynamical boundary value equations associated with the density profile of the lithosphere and the driving mechanism are then considered. To achieve these results, a program is presented to define the physical constants of the earth's material which parametrize the hydrodynamic equation in the microscopic solid state behavior of the crystals of the lithosphere. In addition, to lay the foundation for a generalized geodynamic theory in Earth Physics, specific research areas are considered such as the nature of the kinetics of the phase transitions in mineral assemblages, the equilibrium thermodynamic properties of crystals which are major constituents of mineral assemblages, and the transport properties of pure crystals which are major constituents of mineral assemblages.

# CONTENTS

	<u>Page</u>
List of Contributors . . . . .	iii
ABSTRACT . . . . .	v
I. INTRODUCTION . . . . .	1
II. OBJECTIVES . . . . .	6
A. Program on Earth Dynamics . . . . .	6
1. Program for Better Understanding of the Lithosphere . . . . .	6
2. Program for Core Studies . . . . .	9
3. The Earth as an Elastic Body . . . . .	10
B. Goals . . . . .	13
1. Plate Tectonics and Deep Focus Earthquakes . . . . .	13
2. Volcanism and Faulting . . . . .	18
3. Localization of Mineral Resources . . . . .	20
4. Density Profile of the Lithosphere and Driving Mechanism . . . . .	21
III. THEORETICAL AND EXPERIMENTAL SOLID-STATE PHYSICS AND STATISTICAL MECHANICS APPLICATIONS PROGRAMS . . . . .	29
A. Mathematical Geophysics . . . . .	36
1. Mathematical Aspects of Plate Tectonics and the Mantle . . . . .	36
2. Seismic Profiles . . . . .	36
3. Source Shapes . . . . .	39

## CONTENTS (continued)

	<u>Page</u>
B. Experimental Physics . . . . .	40
1. Description of the Techniques . . . . .	42
2. Acoustics: Ultrasonics and Resonance . . . . .	45
3. State of the Art: Phase Transitions . . . . .	48
4. Types of Transitions . . . . .	55
5. Samples Proposed for Study . . . . .	58
6. Equipment for the Program . . . . .	59
7. Initial Experiments . . . . .	59
C. Theoretical Physics . . . . .	64
1. High Pressure Melting . . . . .	64
2. Lattice Gas Theory . . . . .	67
3. Theory of Solid-Solid Phase Transition . . . . .	68
4. Solid-Liquid Phase Transitions . . . . .	68
5. Theory of Liquids Under High Pressure . . . . .	69
6. Kinetics of Phase Transformations . . . . .	69
7. Condensation . . . . .	71
8. Theory of Magnetic Materials . . . . .	73
IV. CONCLUSIONS . . . . .	74
V. REFERENCES . . . . .	77

# EARTH PHYSICS AND PHASE TRANSFORMATIONS PROGRAM: A CONCEPT AND PROPOSAL

## I. INTRODUCTION

The U.S. Geodynamics Committee\* recently announced a preliminary statement in which a new development of basic concepts in geodynamics is reviewed and various methods of approach toward the better understanding of the processes taking place in the lithosphere are proposed. (EOS, Transaction, American Geophysical Union, Vol. 52, No. 5, May, 1971).

It would be worthwhile to quote some of the paragraphs from the preliminary statement because by doing so it is possible to review the present status of geophysics clearly and concisely.

"Five years ago no one would have predicted that micropaleontologists, geomagnetists, marine geomorphologists and seismologists would be working together to supply the crucial test of a concept comparable to that of the Bohr atom in its simplicity, elegance, and ability to explain a wide range of diverse observations. Yet this convergence of disciplines has occurred during a period of only five years; the result has been a revitalization of the earth sciences comparable to that which swept physics at the beginning of the century. It seems reasonable to predict that as earth scientists gain greater insight into the

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\* The U.S. Geodynamics Committee, which consists of ten members, was established by the National Academy of Sciences to serve as the U.S. National Committee for the Geodynamics Project. The Geodynamics Committee was established under the Geophysics Research Board in collaboration with the American Geophysical Union (USNC-IUGG), U. S. National Committee on Geology (USNC-IUGS), and Ocean Affairs Board (USNC-SCOR).

processes that control earthquakes, volcanic activity and the localization of mineral deposits, they will be able to contribute useful information to society with greater accuracy and confidence than is presently possible."

It is further pointed out in the preliminary statement that in view of remarkable advances made in our understanding of the origin of earthquakes, volcanism, faulting, and mountain building it is now time to take a second look at the new ideas. The unifying concept behind these advances has been the group of ideas known as sea-floor spreading, plate tectonics, and global tectonics. One of the most important insights of recent years is the recognition that tectonic activity on a global scale is concentrated in relatively narrow zones forming a network that surrounds large areas of relative quiescence. Much of the world's earthquake and volcanic activity, and important portions of its minerals resources are concentrated in the active zones. The recognition of an ordered global distribution of present volcanic and seismic activity has been one of the prime factors in the development of the concept of plate tectonics. As a result of geologic work on the continents and several decades of reconnaissance in the oceans, a broad delineation of crustal plates has now been obtained, and three types of interactions at plate boundaries are recognized: diverging boundaries (rift zone), colliding boundaries (underthrusting, trenches and island arcs and perhaps zones of major compression and uplift) and strikeslip boundaries involving only minor convergence or divergence of plates.

One of the important research directions for the next decade is to seek an understanding of the forces involved in the vertical and horizontal motion of the lithosphere. A complete description of the geodynamics processes within the planet is presently beyond our grasp. However, there are a number of areas of research that will lay the foundation for a generalized geodynamic theory. These may be classified insofar as geodynamics is concerned into the following questions.

What is the nature of the kinetics of the phase transitions in mineral assemblages?

What are the equilibrium thermodynamic properties of crystals which are major constituents of mineral assemblages?

What are the transport properties such as the electric conductivity magnetic susceptibility, dielectric constant, visco-elasticity, heat conductivity, etc. of pure crystals which are the major constituents of mineral assemblages?

It is fortuitous that recent advances in the fundamental understanding of solid state physics and statistical mechanics can be applied to these geophysical problems with good promise of success.

Another geophysical phenomenon of importance is polar wandering. From the observational point of view, a central problem of paleodynamics is to determine the past locations of the earth's rotation axis relative to the main plates of the lithosphere, and of these plates relative to each other. Rates of relative movement of the plates are important as one of the main boundary conditions for

theories of geodynamics. Shifts of the poles are important to an understanding of the earth's climatic history and of the response of organisms to variations in world climate. For example, it appears that a necessary condition for world-wide glaciation may be that a substantial part of the polar regions be occupied by continental land masses. Since petroleum deposits are correlated with tropical vegetation in prehistoric epochs, it is important to know what continental regions, which now may be polar, were once equatorial.

The most important part of our knowledge about polar wandering comes from the information contained in the paleomagnetic record of past directions of the geomagnetic field. With modern experimental techniques, ancient positions of the earth's rotational axis can be determined paleomagnetically with an accuracy of  $5^\circ$  or better, provided that suitable samples can be found. If no relative movement had occurred between lithospheric plates, a polar wandering curve common to all the plates would be determined by worldwide paleomagnetic studies. Present evidence indicates no such common curve for the earth as a whole. Therefore the complete determination of the polar wandering problem requires the paleomagnetic sampling of rocks of all ages from all the plates, with good control of the ages of the rocks sampled. The scientific importance of additional work in this field is substantial, both for determining ancient latitudes that may be compared with paleoclimatic data and for determining past positions of the plates. Terrestrial magnetic field reversals in past geological epochs may also have implications for biological evolution thru changes

in the cosmic ray flux. The thermodynamic analysis of magnetic samples found in the earth must be more thoroughly investigated.

## II. OBJECTIVES

### A. Program on Earth Dynamics

The program on earth dynamics is one which is intended to be a laboratory program in "earth materials" and their dynamics in conjunction with a theoretical program on these materials as well as on the theoretical studies in geophysics. The emphasis of the experimental program is to obtain data in the laboratory, particularly data on physical quantities like specific heat, compressibility, elastic constants, electrical resistance, diffusion and melting under high pressures which can be used in models of the earth, its crust as well as its interior. Supplemented by the laboratory information computer models will be constructed using either the data already available or obtained from the experimental work in order to be able to predict such important observations as seismic wave disturbances by the internal restructuring of the earth. It is important to note that the laboratory efforts need to be extended in two ways: measurements at simultaneous high pressure and high temperature should be made, and the volume capacity of high pressure facilities should be increased to allow measurements of physical properties important to geodynamics. (See Figure 1).

#### 1. Program for better understanding of the Lithosphere

Work in recent years has shown that tectonic activity is concentrated in relatively narrow zones. These strips form a network which surrounds "islands" of relative inactivity. These islands or crustal plates are fairly well mapped out and much is known about the behavior at the boundaries: whether they are

diverging, colliding or slipping. These boundaries form an extremely interesting object for the study of laboratory physics. An estimate of the velocities of the motion of the plates will lead to an extremely interesting viscous-hydrodynamical problem. This problem leads itself very nicely to a model study. The idea is the following, we start to research for plastic materials that have the same viscoelastic properties as the materials found between the plates. At many laboratories, chemists have been able to tailor-make materials with almost any range of properties. By moving hard objects in the shape of the plates in the appropriate directions, one could try to reproduce the flows that take place in the rifts. To obtain the stresses and flows one could use polarized light, X-ray or ultrasonic probes. Equipped with this type of information one could then try to establish mathematical models for the motion of the matter in the rifts.

One of the main pieces of information needed for the actual study of the static behavior in the rifts is the temperatures, densities and pressures as a function of space in the material in the rifts and plates. The prime source has always been seismic data. Unfortunately, seismic data give velocities of sound and not density proportional to temperature and pressure. Much laboratory work will be needed to establish whether one could reproduce the velocities of sound with materials most likely to occur in the lithosphere at the pressures we expect to be present inside the earth's crust (Reference 1). Hence low frequency ultrasonic measurements should be undertaken at high pressures in conjunction with an attempt to make a theoretical model to explain the velocities and attenuation.

At k bar pressures the atoms are located on the steeply descending part of the potential curve that describes the pair-wise interaction. This has the consequence that the ordinary harmonic behaviour (which is the result of an interplay between the repulsive and attractive part of the potential) has totally disappeared. The result is that the solid behaves more and more like a hard core liquid. And, indeed, not surprisingly, it is known experimentally that many crystalline solids are showing a phase transition back into the liquid state at very high pressures.

It is an open question whether these liquids have an equation of state and elastic moduli similar to ordinary liquids. There is every reason to expect that liquid state of aggregation is more comparable to liquid mixtures, than to pure liquids. Since the mixtures of two liquids do not always have properties that are the simple superposition of the properties of each component, there is a justification to undertake a serious study of liquid mixtures at high pressures. Bridgeman has already pointed out that liquids at extreme pressure have some unusual and new properties (Reference 2). There are similar indications from shock tube work.

Another form of geological liquids are the high temperature normal pressure liquids as found in lava. It would be of interest to find out whether adiabatic decompression gives indeed the temperature of molten lava. In other words if the pressure is suddenly released how does the state of the liquid travel on the P. V. T. surface.

## 2. Program for Core Studies

Seismic waves are to the core-geophysicists what electromagnetic waves are to the nebuleastronomer: his only source of information. There is of course one exception, the magnetic field on the surface of the earth is mainly due to the flow in the core and gives one additional piece of information.

If we consider the simplest model of the earth: a mantle and a core, without any further subdivisions then we can broadly classify two types of ray paths: through the mantle only and both through the mantle and the core. Since there is refraction and reflection at the boundaries and since the ray paths are not straight there is a number of possibilities by which signals from a certain earthquake source can reach their "destination", the seismic station.

One can study the core separately by comparing the travel time of waves that went through the mantle only, with the travel time of waves that went through the mantle and the core. The result of many years of work is that the core itself consists of an outer and inner core which have different properties. The outer core is liquid, and the inner core is most likely solid. Calculations have shown that the velocities in the inner core are about 10% higher than in the outer core and that the change, although not so abrupt as the change near transition from mantle to core, is nevertheless rather sudden. The transition layer is about 200 meters.

The inner core is probably the most fascinating object to study. There are a number of hypothesis made; many ideas are possible since little is known

about the temperature and less is known about the pressure. The temperature range is based on the idea that the presence of a liquid requires at least a temperature above the melting temperature. The temperature of the inner core are estimated between 4000 and 5000°K and pressures have been calculated to be  $10^6$  atm.

The problem is to construct a form of matter on paper that exists at these densities and temperatures by taking into account all knowledge of atomic and nuclear structure. Wigner has already described that would happen if electrons can no longer be considered to be associated with an individual nucleus. He applied this idea to high density hydrogen, and a similar phenomenon should take place in heavier elements leading to a form of matter different from the properties we are accustomed to. This part of the program would be entirely theoretical.

### 3. The Earth as an Elastic Body

The overall properties of the mantle of the earth have been described by the usual set of moduli for an isotropic material. For most parts of the mantle Poisson's ratio is about 1/4, which accidentally leads to a mathematically convenient solution of the equations for the Rayleigh waves. These moduli were used by Love in 1911 to describe the body tides of the earth.

If the earth were rigid, the axis of rotation would make a constant nutation (Chandler period). It is well known from observations that this period is not constant, but oscillates around a value somewhat different from the predicted

value. These deviations are due to the elastic behaviors. The relation between this period and the rigidity of the earth has been determined. The problem of predicting the nutation however is much more complicated since meteorological and oceanographic processes play a role which is not very well understood.

A theoretical study should be made to see whether sufficient meteorological and oceanographic data is available to attempt a correlation between the motion of air and sea masses and a part of the wobble. It may be that the other possible processes as the plastic relaxation of the tidal "flexing" of the earth may show a periodic or quasi periodic behavior so that if the air and sea motions are subtracted, a regular pattern may be found.

Additional work on the tides of the earth is proposed independently of the study of the polar wandering. The tidal forces on the earth are usually studied by measurements of the vertical displacement change in strength and direction of gravity. However very little work seems to have been done to detect diurnal motions in the horizontal plane. This is feasible with lasers for distances of the order of kilometers, and microwave links for longer distances. Such work could be done by using the facilities available from existing commercial and military microwave stations.

The elastic properties of the mantle are related to the elastic properties of the individual materials that make up the mantle. The connection between these physical quantities forms a very difficult problem. There are two steps in which this problem has to be solved.

The first problem is mainly a question of observation. What is the distribution of sizes, packing and orientation of crystal pieces and voids in the material? If such a distribution is available there is a much harder question to be tackled: how should one calculate the average elastic constants? Such a problem has until now been considered only from the point of view of setting upper and lower bounds (Reference 3). It must be possible to describe this problem in terms of the previously described distribution. The equation governing the elastic behaviour of an anisotropic medium is a second order differential equation containing the space dependent elastic constants. Such an equation has a Green's function solution, which after appropriate rewriting leads to an integro-differential equation for the displacements of the medium. Inserting a trial solution leads to a hierarchy of equations which, if truncated, yields a solvable set of equations. The best possible equivalent elastic constants are determined this way. The refinements depend mainly on the amount of effort one wants to spend, that is how many equations one decides to solve (depending on the step at which the hierarchy is truncated).

In order to determine the direction of an incoming signal one must use an array of detectors which are electronically coupled in such a way that the phase differences are properly registered. Such an instrument is somewhat analogous to what has been used in radio astronomy and can be adapted to the wavelengths by placing the transducers on mobile equipment.

In principle it is possible to build up enough resolving power to locate the course of the waves, in particular the size and shape of the region in which the waves are produced. Arrays should have the size of 20-100 Km. in order to give enough resolving power. However there is an enormous obstacle: The earth is not like the ether, a homogeneous isotropic medium! This means that a preconceived notion about the velocity of sound as a function of the coordinates in the earth (mantle and core) is necessary. Fortunately one can look at the source from different sides.

## B. Goals

To understand the geophysical phenomena such as plate tectonics, polar wandering and volcanism, it is necessary to solve the formidable problems of the macroscopic hydrodynamical boundary value equations. Geophysicists and hydrodynamicists have made excellent progress, especially in recent years, in the macroscopic analysis. However, without the knowledge of the physical constants of the earth's material which parameterize the hydrodynamic equation, in the microscopic solid state behavior of the crystals of the lithosphere, no complete understanding will result.

### 1. Plate Tectonics and Deep Focus Earthquakes

In the theory of plate tectonics, the outer 50 to 100 kms of the earth is assumed to consist of a number of segments of rigid shells in motion relative to one another. The sea floor is believed to be created along the oceanic ridges which form raised linear features across the earth's oceans with the total surface

area conserved by underthrusting of the plates in trench-island arc areas.

This theory has been strikingly successful in explaining a great deal of observational information, both geophysical and geologic, such as the linear magnetic anomalies in oceans, the distribution of earthquakes, and the youthful age of sediments in oceans.

However, as earth scientists have moved rapidly forward to fit more and more observational data into the framework of the plate tectonic theory and to refine it, one important element has been missing. This has been a fundamental understanding of the origin of the forces that cause and maintain the plate motions.

A subject of great interest in geodynamics is the source of earthquakes. Not the location, but the triggering mechanism. Do tensions accumulate in a certain region near fault lines and are suddenly released or do we deal with retarded phase transformations? This is apparently still unresolved.

We will discuss two hypothesis: super cooling and the "lubrication" theory. If the supercooled phase transitions play a role then it would be worthwhile to try to create these in the laboratory. How much energy can one expect to be released from a retarded phase transformation? That raises the question-how far a metastable state can be removed from the normal (equilibrium to equilibrium) phase transition. Suppose certain regions have the right T, P and density for a phase transition to take place, but that the time scales at high pressures are different from the scale at one atmosphere, or suppose that the condensation

nuclei would be lacking in order to catalize the process. Under such circumstances one could obtain considerable undercooling. Such a retardation of the transition leads to an explosive transition as one can show with simple laboratory experiments with very purified molten paraffin. One should investigate theories for undercooling and superheating of molten rock in combination with the methods or techniques of nonequilibrium statistical mechanics. For ordinary liquid-solid transition this has been done by Schneider (Reference 4). An extremely simple model can be obtained by comparing the van der Waals isotherm with the Andrews isotherm. The experimental data will give the curvature of the isotherm above and below the flat part for temperatures below the critical temperature. From this one can construct the minima and maxima of the van der Waals oscillation as a function of the temperature. This can be linked to the barriers found in the diffusion constant. Such crude theories can of course be augmented by making use of the molecular field of similar theories, where the free energy is estimated and one can use Landau's idea to associate the second derivative of the free energy with the relaxation time associated with the transition.

The second type of theory that has been proposed is the idea that large rock masses under shear stress do not move as long as the forces are unable to overcome the initial friction, but that the friction could be considerably lowered if fluids penetrate the masses. This lubrication would make it possible that the stresses are suddenly released. This theory seeks confirmation in the

correlations between earthquakes and new water reservoirs (Reference 5).

To understand this better one should study the physics of fluids in porous media. This is a very difficult field, but fortunately experiments at high pressures have been performed.

Mechanisms likely to be responsible for the attenuation of seismic waves have been recently reviewed by Anderson (Reference 6). He tries to fit the data with an exponential temperature dependence and an inverse frequency dependence for the loss per cycle, denoted by  $Q^{-1}$ . He also gives a large amount of data for  $Q^{-1}$  as obtained by a large number of different investigators for each of the known seismic waves modes. There are three reasons to consider  $Q^{-1}$  rather than  $Q$ . (1) If the wave travels through several regions with different anharmonicity, the  $Q^{-1}$ 's give the proper average. (2) If two or more mechanisms are competing, the  $Q^{-1}$ 's can be added. (3)  $Q^{-1}$  is a direct measure of the deviation from the ideal elasticity.

Apparent attenuation takes place due to geometrical effects resulting in a loss in amplitude in the direction of the path, which is simply due to scattering at the direction of the ray. Such a quantity cannot be measured separately but one could make a crude theory provided one could obtain some information from other sources or make hypothesis about the gradients of the inhomogeneity of the material that makes up the mantle or the core. Work has been done on sandstone, shale and soils (Reference 7).

Next in importance comes the question about the (actual) attenuation on a microscopic scale. The literature in Solid State physics breaks up in two groups: attenuation via motion of grain boundaries, moving interstitials or dislocation lines at one hand and atomistic processes, where the energy is transferred to another degree of freedom, at the other hand. The first class is often rather phenomenological, the second class not, contrary to a remark in the review article. Also we disagree that all this data is only of interest for low temperature work. In particular in the first class the temperature influence depends largely on free energy barriers which are of importance up to the melting temperature.

Before we go to the microscopic mechanism, we mention one submacroscopic mechanism which may play a role: the dissipation of energy by friction along small cracks. Such a mechanism will at very high pressure eventually disappear and hence it may not be a major contribution to the attenuation of waves in the mantle. It would be influenced by the presence of water or oil. If the material is free of cracks but polycrystalline, we may have stress relaxation in grain boundaries and/or motion of the walls.

High pressure sound attenuation in homogenous material is usually attributed to the irreversible motion of dislocations (amplitude dependent) or due to simple relaxation mechanism. The last group can be recognized by the Debye-like frequency dependence of  $Q^{-1}$ . Such models are often combined with the "free energy of activation" G models, in which case one can obtain a temperature and frequency

dependence with the pressure dependence as a parameter in  $\Delta G$ . One can speculate about the meaning of  $\Delta G$ , but even if the free energy is not interpreted this model has the advantage that one can extrapolate to higher pressures from relatively modest pressures. Again, computer models are desirable for the study of surface and other guided waves in a layered structure. Since it is known that the velocity of longitudinal and transverse waves on the earth changes with the depth, the possibility exists of wave propagations which are similar to surface waves. These are called guided waves or Love waves. When an earthquake takes place the source is most likely comparable to a point source and the question is—how much is radiated in each space angle. This is not trivial if the source is situated in a stratified layer. One could make a relatively simple computer model using a three dimensional grid, in which the velocity is only dependent on  $Z$ , the coordinate perpendicular to the surface and simulate the point source by a strong deviation of a certain point. One can then subsequently detect the influence at certain selected points on a sphere around the origin—source.

The type of work has been done for actual problems in a rather different way.

## 2. Volcanism and Faulting

Between the rift zones where new lithosphere is created and the collision zones where lithosphere is destroyed lie the stable plates. These areas are relatively tranquil but not absolutely so; movements, mainly vertical, take place; volcanism, localized but often extensive, occurs.

In addition, earthquake activity is uncommon except in the vicinity of volcanic regions. The concept that all deformation takes place at plate edges is incorrect. Important deformations by faulting and vertical movement occur - and may even be initiated - at great distances from the plates edges. Nearly all volcanism resulting in the formation of sea - mount clusters and groups of volcanic islands appears to begin at a relatively late date after the formation of new crust. The nature of this volcanism seems to be different from the process of formation of new crust at the divergent edges of plates. Volcanism may be more closely related to smaller scale deformations of the underthrust plates themselves than to the mechanism causing the underthrusting.

Within plates, volcanism, vertical motion, faulting, and intrusional activity occur in many localities, usually without causes directly attributable to broad plate motions.

The structural response of the upper portions of the earth crust to forces below the plates appears to be strongly modified by mechanical inhomogeneities of the crust and by the past history of deformations. Studies on some fracture zones have shown that their structure is influenced by recent changes in spreading direction resulting not only in changes in trend, but also in the occurrence of rifting at high angles to the plate edge and in the formation of new crust in these tectonic features that are elsewhere volcanically passive.

Hence, such studies should emphasize not only the tectonics, but also the chemical and physical nature of the lithosphere.

### 3. Localization of Mineral Resources

One of the most important insights of recent years is the recognition that tectonic activity on a global scale is concentrated in relatively narrow zones forming a network that surrounds large areas of relative quiescence. Much of the world's earthquake and volcanic activity, and important portions of its mineral resources are concentrated in the active zones.

On the matter of plate tectonics, there are indications of largely synchronous vertical movements within plates and at plate boundaries. The chronology of such displacements between and within plates is important to a full understanding of tectonic dynamics.

Many of these vertical movements within tectonic plates are of such magnitude that they would seem to require large volumes of lateral mass transfer within or beneath the lithosphere.

These vertical movements, both within plates and at their boundaries, control the distribution and occurrence of many of our important mineral resources. The fact that oil and gas are present only in sedimentary rocks restricts their occurrence to areas that have subsided enough to accumulate these deposits, normally near areas that have been uplifted enough to provide a source of erosional detritus. Similarly, many economic mineral resources of metamorphic origin require a history of significant vertical subsidence and subsequent vertical uplift to bring them to accessible depths.

One of the most significant features of the earth's lithosphere is the contrast between the crust of continents and the crust beneath the deep oceans- in the thickness, age, tectonic history, and bulk composition. The transition between these crustal types is one of the most fundamental features of the earth and one of the longest.

The area of transition between continental and oceanic crust is generally considered to offer an important opportunity to meet the greatly expanding energy demands of mankind. Large amounts of oil and gas have already been discovered within continental margins, and an improved understanding of these areas will assist in developing these resources.

#### 4. Density Profile of the Lithosphere and Driving Mechanism

The lithosphere includes the crust and the portion of the upper mantle that lies above the low-velocity zone. Its physical properties are a function of depth (they also vary laterally): they are dependent upon chemical composition and physical conditions. The lithosphere is divided by major discontinuities, both vertically (i.e., by essentially horizontal discontinuities, particularly the Moho) and laterally, especially in the seismically active belts.

The lithosphere is distinguished from the underlying asthenosphere primarily on the basis of differences in physical properties, particularly rigidity, as determined from studies of seismic wave propagation. The upper surface of the lithosphere is well defined except where it appears to be thrust into the asthenosphere; in these areas it can be related to seismicity. Its lower surface

is known only in a general way over most areas, but in the areas of underthrusting it may be definable in some detail through seismicity studies. The lower boundary, is not at all distinct in a number of critical areas both at boundaries of lithospheric plates and within the areas themselves, nor is there any assurance that it remains fixed with time. In fact, one would suspect that the opposite is true; that differential movements that have occurred within the lithospheric plates must be related to the dynamic nature of the lower boundary.

The fact that the lower boundary of the lithosphere is the most significant discontinuity that is involved in the plate tectonic concept means that determining its nature, character, and variations with time are fundamental to understanding and testing the concept. New geophysical techniques may be required to deal with this problem.

It has now been proposed, as a result of work done during the Upper Mantle Project, that the density profile of the earth has a minimum somewhere near the lower boundary of the lithosphere. This creates a gravity potential that should tend to drive matter toward the surface. It is generally agreed that there is a minimum in shear velocity that occurs near the lithosphere boundary. There are many indications that this minimum results from a zone of partial melting; that is, matter at a certain depth is partially melted but solidifies above and below this depth. It is generally agreed that the interior of the earth has certain zones in which there are jumps in density caused by phase transformations. These conditions, accompanied as they are by pressure and temperature gradients should lead to hydrodynamical instabilities.

The experimental work in the kinetics of phase transition is just beginning. The importance of the subject is well illustrated by the history of the production of artificial diamonds. The reaction graphite-diamond requires a geological epoch for completion in many regions of the diamond stability field, unless it is accelerated by the addition of a catalyst. Water is known to accelerate transformation of silicates in the laboratory. Water content, in very small amounts, in the earth may be crucial to the time scale of phase transformations that in turn affect the geodynamic boundary conditions. Here, too, model systems will be invaluable in simulating such processes.

At this moment the relations between the solid state properties of mineral crystals and the driving mechanism of plate tectonics must be clarified more specifically. As mentioned previously, all physical properties must be known either experimentally or theoretically over a wide range of temperature and pressure. Also, many mineral crystals undergo phase transitions under high pressure. Especially for these dynamical properties the time dependence must be investigated.

There are a variety of mineral crystals in the mantle. However, these crystals may be regarded as different combinations of only a couple of compounds, i.e. magnesium oxide,  $\text{MgO}$ , and silica,  $\text{SiO}_2$ .

Some of the leading questions we therefore would like to ask are:

## 1. Solid-Liquid Transitions.

What are the melting temperatures of the magnesium-containing pyroxenes, olivines, and spinels at pressures corresponding to those in the mantle: i.e., up to 1400 Kb?

Many crystals are known to have more than one phase transition at a given temperature, i.e., liquid-solid (at a lower pressure) and solid-liquid (at a higher pressure). The mechanism of the latter, the so-called high pressure melting, will be discussed in a later section.

## 2. Solid-Solid Transitions (Polymorphic Transition)

(a) What phase transitions are there involving the more common silicates at the temperatures (100°C–500°C) and pressures (2 – 15Kb) that might exist at the crust-mantle boundary?

(b) What phase transitions exist involving silica and magnesium olivines, pyroxenes, and spinels at the pressures prevailing in the mantle (10 – 1400 Kb)?

The various minerals which are compounds of the oxides believed to be the most likely constituents of the mantle, magnesium oxide (MgO) and silica ( $\text{SiO}_2$ ), require high pressures to undergo phase transitions. A transition that has been attained in the laboratory is that of silica of quartz density (density  $2.6\text{gm/cm}^3$ ) to coesite ( $2.9\text{ gm/cm}^3$ ) at 27 Kb and 700°C or 39 Kb and 1750°C; another transition of silica to stishovite (density  $4.3\text{ gm/cm}^3$ ) at 139 Kb and 1600°C. Both the olivine ( $\text{Mg}_2\text{SiO}_4$ ) and pyroxene ( $\text{MgSiO}_3$ ) forms of magnesium silicates require pressures higher than those attainable in static experiments to be converted into

spinel or spinel plus stishovite forms. Hence some sort of extrapolation is required.

At this point it should be emphasized that scaling laws exist which may make the necessity for extremely high pressure data less crucial. This means that if two different atoms A and B in two different systems interact with the same law of force except for the difference in the scaling, then the equations of states of two systems are identical except for a scale. Since there are many different types of interactions even if the chemical formulas are similar there are as many different laws or corresponding states. The different laws of corresponding states, therefore, must be found experimentally and theoretically for different classes of materials.

One type of scaling is to replace some of the metal elements in these compounds by other metals of equal charge and larger ionic radius. A phase transition should then be made more easily because the transition essentially depends upon attaining a certain ratio of the radii of the constituent atoms. The zero-pressure ion radius of silicon is  $0.42 \text{ \AA}$ ; the next +4 element in size upward from silicon is germanium, of radius  $0.48 \text{ \AA}$ . The zero pressure radius of magnesium is about  $0.68 \text{ \AA}$ . The next one up of +2 charge is nickel, with about  $0.70 \text{ \AA}$  zero-pressure ionic radius.

A series of experiments at  $600^\circ\text{C}$  and 0-90 Kb was carried out on various mixtures with various ratios of  $\text{Ni}_2\text{GeO}_4$  to  $\text{Mg}_2\text{SiO}_4$  by Ringwood and Seabrook (Reference 8) and a substantial reduction of the pressure of the phase transition has been observed.

As was mentioned earlier, there seems to be a zone of partial melting at a certain depth in the mantle. It turns out however that the high temperature melting is a rather prevailing phenomenon observed in many different substances. Examples of such substances are barium, tellurium, europium, antimony, carbon, the intermetallic compounds  $\text{Bi}_2\text{Ti}_3$ ,  $\text{Sb}_2\text{Te}_3$  and  $\text{PbTe}$ , and inorganic salts  $\text{KNO}_3$  and  $\text{KNO}_2$ .

Since in liquid phase atoms are arranged randomly in space, while in solid phase atoms are arranged regularly on a crystalline lattice, the phenomenon of melting can be regarded as a transformation from a state of ordered arrangement to that of disordered arrangement of atoms. Lennard-Jones and Devonshire (Reference 9) applied the theory of order-disorder transformation in binary alloys to the phenomenon of melting and explained various equilibrium properties at the melting temperature rather successfully. It is obvious, however, that a straightforward application of Lennard-Jones-Devonshire theory does not explain the possibility of having two phase transformations, one at a lower pressure and the other at a higher pressure.

Quite recently Yoshida and Okamoto (Reference 10) formulated a theory of high pressure melting. They argue that if the interatomic interaction potential has a slowly increasing repulsive part, it is possible to have a random arrangement of atoms at high density, i.e., the high pressure. Their theory is a direct application of L-J-D theory except for a modification of the interatomic potential. Their prediction of the melting curve is semi-quantitatively good and explains the observed data of Rb and Cs reasonably well.

Further improvement and extension of the theory of high pressure melting along Yoshida-Okamoto's idea is promising, and improvement can be made by the following steps.

(a) L-J-D theory is one of the crudest approximations of the order-disorder transformation, i.e., the one-body approximation, and hence the semi-quantitative agreement with the data on Rb and Cs is very likely to be fortuitous. To predict the melting curve, the relation between the melting temperature and pressure, more accurately and calculate other equilibrium properties, such as the latent heat of fusion, consistently, one has to extend the theory to include the two-body and three-body correlations. Investigation along this line is promising.

(b) The L-J-D theory deals only with equilibrium properties and there is no way of calculating dynamical quantities. This can be achieved by modifying the Hamiltonian so that the kinetic energy terms are included. In this way one cannot only improve the calculation of equilibrium properties but also can calculate the velocity of sound in the neighborhood of the melting temperature.

(c) In the L-J-D theory, the assumed solid structure is already built into the formulation. This more or less ad hoc, assumption can be eliminated if one goes to at least three-body or even as many as ten-body approximations which is entirely within our reach with the high-speed computer facilities. The expected numerical result would be very accurate as long as the assumed interaction potential is appropriate. This calculational technique will in turn be used in order to determine the nature of the repulsive part of the interaction potential, which is the least known information at present.

A remarkable progress has been achieved in the understanding of the mechanism of solid-solid phase transformations. This is achieved especially in the area of ferro-electric phase transformations. In ferro-electric crystals the motion of dipole moments is associated with the optical mode of lattice vibrations. By experimentally observing the motion of dipoles by optical techniques one is able to observe the behavior of optical modes as the phase transformation point is approached. It has been established recently that the ferro-electric phase transition is a direct consequence of the freezing of some optical modes at the transition point. This means the frequencies of some optical modes (shear modes) decrease steadily and finally vanish (freezing) at the transition point. Those optical modes whose frequencies vanish at the transition point are called "soft modes". Ferro-electric crystals are most suitable to detect the soft modes because electric dipoles are good probes. It is now commonly agreed that the solid-solid phase transformation is always accompanied by the freezing of soft modes even in non-polar crystals. This means, in turn, that the analysis of the optical branch of lattice vibrations is essential in order to understand the mechanism of solid-solid phase transformation. Dynamical theory of lattice vibration has been developed to a very satisfactory degree in the past twenty years and we are now able to calculate the spectrum of lattice vibrations even for rather complicated crystals. Investigation along this direction must be further encouraged with an extensive use, again, of high speed computers.

### III. THEORETICAL AND EXPERIMENTAL SOLID-STATE PHYSICS AND STATISTICAL MECHANICS APPLICATIONS PROGRAMS

The ultimate goal of theoretical solid-state physics and statistical mechanics is to predict both the equilibrium properties and dynamic properties quantitatively from the known properties of atoms and the laws of forces between atoms. By the equilibrium properties we mean the properties such as the equation of state (the relation between the pressure, volume, and temperature), the specific heat, the static dielectric constant, static electric conductivity, etc. Those properties are observed in gases, liquids and solids which are in thermodynamical equilibrium. By the dynamic properties we mean, here specifically, the properties which represent responses of physical systems to externally applied forces which depend upon the time. Any response which depends upon the way in which the external force is applied (either very slowly or very rapidly) is called the dynamical response, and the parameter characterizing the response is called the dynamical property. Examples of dynamical properties are the electric conductivity, magnetic susceptibility, viscosity, thermal conductivity, diffusion constant, etc. Those properties are functions of frequencies of the external field.

Since the basic theory of statistical mechanics is so firmly established, there is no ambiguity, in principle about how to calculate both the equilibrium and dynamic properties. The equilibrium properties are all derivable from the partition function or sometimes more directly from the free energy of the system,

and the free energy is expressed, very concisely, in terms of the Hamiltonian for the physical (macroscopic) system under consideration. All dynamical properties are, likewise, calculated or rigorously expressed as the Fourier Transform with respect to the time variable of the pertinent time dependent correlation functions.

As a matter of practice, however, there are almost insurmountable difficulties, one of a mathematical nature and the other of a physical nature. The former, which is often called the many body difficulty, is due to the fact that any macroscopic system is made up of an enormous number -  $10^{23}$  per mole - of atoms and molecules. The latter, which is of a physical nature, represents the fact that the Hamiltonian of the system or, more specifically, the laws of interaction between atoms or molecules are not known precisely enough. In order to overcome these difficulties two types of approximations, corresponding to two types of difficulties, are introduced. The first is a mathematical approximation and the second is a physical approximation. Fortunately, however, remarkable progress has been achieved in the past twenty years in attacking the many body difficulty. It is now possible to calculate any physical quantity successively more accurately as long as enough time and effort are devoted. An extensive use of modern high speed computers is almost tacitly assumed.

The second approximation means that the Hamiltonian of a system is always an approximation to the actual physical system. In this sense, in theoretical treatments, we are always dealing with some sort of model systems. As a result

of establishment of quantum mechanics around 1925, however, this difficulty presents a less serious problem.

Let us now briefly examine the various experimental techniques available for the study of solid state properties under both high pressure and temperature. The technology of ultra-high pressures ( $>100$  kbar) as a controlled environment for experimental work on materials has now advanced to the stage where a very comprehensive literature is available.

The essence of the problem can be summarized as follows. A linear force (produced by some sort of hydraulic press) travels through a certain linear displacement, at the same time reducing the volume of the experimental sample so that a high (hopefully uniform) pressure is attained. From the technological viewpoint, the difficulty lies not so much with the production of the force (usually several hundred tons) as in the successful containment of the sample within the prescribed location. The present state of the art has been attained by the use of suitable materials (e.g. tungsten carbide, carb alloy, and various hardened steels) for the pressure vessel walls and the ram which applies the pressure. Careful attention to the geometry of these components to achieve suitable pressure gradients, and the use of suitable materials (pyrophyllite, talc, various plastics) as pressure-transmitting media, seals and extrudable gaskets. When solids are involved, uniformity of pressure is of course not guaranteed on account of friction; lubricants such as molybdenum disulphide have been used to reduce this effect. The upper limit of pressure reported by most workers is of

the order of 100 – 500 k bar, the maximum available pressure being determined by rupture of the gaskets of containing vessel.

The calibration procedure most commonly used utilizes reference materials (e.g. bismuth) which undergo easily detected phase transitions at known pressures.

Heating of the sample is most readily carried out by means of an electric current, either through the sample itself (for a metal) or by means of a conducting tube surrounding the sample. Temperatures greater than 3000°C have been achieved in this way for long periods.

A productive program would be to study selected crystals using some simple probe such as conductivity to locate the positions of phase changes in pressure and temperature and then simultaneously to obtain molecular spectra from laser Raman scattering on approaching the transition lines from phases found in order to characterize the crystal symmetry and local order of the phases. By studying the low frequency region ( $10$  to  $100\text{ cm}^{-1}$ ) of such spectra one can hope to identify the motions involved in the cooperative behavior in the transition and the temperature-pressure dependence of the phase transition dynamics.

There is a large body of recent work on the lattice dynamics of phase transitions emphasizing the importance of "soft modes," modes which show the onset of instabilities by rapidly decreasing their frequency as a transition is approached. Such theoretical work on instabilities and anharmonicity plus recent experimental confirmations and extensions at low pressure is now ripe for possible extension to high pressure studies.

With the same samples and apparatus high resolution light scattering allows the hypersonic elastic constants to be determined (Brillouin scattering methods). Recent studies of solid phase transitions have shown the importance of the acoustic mode instabilities in phase changes. In particular there are cases of very strong interaction of soft modes and acoustic modes leading to phase changes.

Low frequency ultrasonic measurements (frequencies to hundreds of megahertz) would seem to complement the aforementioned optical investigations. Of particular interest are the shear mode elastic constants near solid-liquid transitions. The importance of determining sound velocities in materials of geophysical interest stems from the fact that sound velocities is one of the few experimental properties whose measurement is not confined to the surface of the earth. The correlation of seismic velocity information with laboratory data on sound velocity in rocks and minerals may be expected to contribute to knowledge of the crust and mantle.

Measurement of elastic constants over the widest range of accessible temperature and pressure contributes to understanding of the equation of state of given materials. The determination of elastic constants with high precision permits extrapolation of data beyond the range of accessible temperature and pressure. For determining sound velocities, three basic methods have been employed with investigation of materials of geophysical interest: resonance, pulse transmission, and ultrasonic interferometry. The choice of a given technique is dictated by the

nature of the specimen under consideration, the ambient conditions (temperature and pressure), and the precision required.

At this juncture ultrasonic experiments at pressures ranging to about 10 k bars have become relatively routine, the experimental difficulties growing rapidly as pressure is extended. Consequently, it is not unlikely that, for the next phase of effort, ultrasonic measurements should be made on synthetically prepared polycrystalline specimens. This permits use of accurate interferometric measurements of ultrasonic velocity, and consequently provides the precision required for determination of reliable pressure and temperature derivatives. Using this approach it has been shown, for example, that from measurements on MgO and  $\text{Al}_2\text{O}_3$  at 4 k bar the bulk modulus at hundreds of k bars could be accurately inferred.

One final class of experiments should be mentioned, those measuring the electrical conductivity. Electrical conductivity may be expected to be a very useful measurement to mark the presence of phase transitions which can then be studied in detail by the methods discussed previously.

Measurements of electrical conductivity can be carried out to very high pressure and temperature because of the simplicity of the probing mechanism. The electric current used to heat the sample can be used simultaneously as the probe of measuring the electrical conductivity by means of the potential drop across the sample.

Measurements have been made on metals up to 425 k bar. Of course the problem of determining the electrical conductivity of insulators such as silica at high pressures will be more difficult because the currents will be much smaller but the change in conductivity near a phase transformation should be large enough to observe.

Laboratory studies must be made along two main lines. Experiments on crust and mantle materials under conditions approximating as closely as possible the actual ambient temperatures and pressures; and experiments on "model systems" in which systems to be studied are designed so as to yield information on a laboratory scale, i.e., laboratory spatial and time scales (- as opposed to "earth" dimensions and times in eons -), which has useful analogies in geophysical phenomena. The search for useful "model systems" could most profitably be directed also to analogues of actual geophysical processes which permit scaling of temperature and pressure to levels more readily approachable in large laboratory volumes than the actual ambient T and P levels in the mantle. The proposed model systems approach suggests itself as a natural - even an essential - complement to the "head-on" attack, since detailed laboratory studies of geophysically significant processes must necessarily involve scaling of some combination of the significant independent variables (e.g., spatial and temporal, and temperature and pressure). It is quite clear that, while the discovery of the model systems themselves will be most challenging tasks for solid state science, current knowledge of the solid state and liquid state has reached such a level of

sophistication as to suggest that the time may be ripe for the development of such an attack in geophysics.

We are now ready to discuss specific methods of approaches to determine physical properties.

## A. MATHEMATICAL GEOPHYSICS

### 1. Mathematical aspect of the plate tectonics and Mantle.

The study of plate tectonics requires the analysis of the response of an inhomogeneous visco-elastic system to a set of forces which arise from the mantle. A plate is an inhomogeneous system because the mineral constitution may vary not only vertically but also horizontally. The temperature of the plate is not uniform. The mathematical boundary-value problems associated with the zones of instabilities within the mantle will be extremely complicated especially because the material constants such as elastic constants, viscosity, and heat conductivity are functions of temperature and pressure. Furthermore, many mineral crystals undergo phase transitions and physical properties change discontinuously even within the mantle.

### 2. Seismic Profiles

Seismic waves provide the primary probe of deep layers of the earth. The utility of seismic waves as a diagnostic tool in yielding detailed information on the crust and mantle depends crucially on the possibility of interpreting data relating to seismic wave properties such as velocity and attenuation. This in turn requires as complete as possible an understanding of the propagation

characteristics - including velocity and attenuation data - of longitudinal and transverse acoustic waves in materials of geophysical interest under a wide range of temperature and pressure.

A great deal of what is already known about the internal structure of the earth has been derived from seismic studies. The seismic frequencies of interest to geophysicists vary from about  $10^{-14}$  Hz to 1 Hz, and the modes of vibration include free oscillations of the earth as a whole, bulk compressional and shear waves, and surface waves. Detailed analysis of transit times for disturbances produced by earth quakes, refraction effects, and the loss of shear modes when passing through liquid regions has helped delineate the principal features of the crust, mantle and core. More recently, precise attenuation measurements (the measure of attenuation used in the literature is the "internal friction" defined above as the loss per cycle,  $Q^{-1} = (1/2N)\Delta W/W$  where  $W$  is the elastic energy per unit volume) have enabled local inhomogeneities in the crust and upper mantle to be revealed and in particular, the existence of a low-velocity (and hence low density) - high attenuation region possibly due to partial melting is suspected. Such a region, if it exists, may well be expected to contribute to the mantle instability which generates the forces responsible for global plate movement.

It is clear that to properly understand the results of seismic experiments and to formulate working models for the earth's interior, data on the earth itself must be supplemented by laboratory analysis of materials representative

of the earth's interior and under conditions (high temperatures; several thousand degrees, and high pressures; up to 1400 kilobars in the mantle) obtained there. Further refinement in the solution of the complicated boundary value problem for the propagation of seismic waves through the inhomogeneous medium of the lithosphere is possible because of the development of modern high speed computers.

Results of laboratory studies of elastic properties as functions of pressure, temperature and approach to phase transitions must be considered in order to test our understanding of the causes of the minima and steps in the velocity profiles. The ultimate test of the correctness of any model based on phase transition theory and laboratory measurements on model materials will be its ability to reproduce the features seen in seismic measurements (arrival times and pulse shapes).

It is felt that seismic (elastic) data and lithosphere motions are largely determined by phase transition phenomena. Thus measurements of velocity and attenuation must be made at simultaneous high pressure and temperature, i.e. in the neighborhood of the possible transitions rather than extrapolated. We propose to do this in both actual geophysical samples and in model phase transition materials. In order to understand the velocity and attenuation data and in particular elastic instabilities such as the onset of flow (or large shear deformation) and velocity minima one must study the phase transition dynamics with emphasis on the coupling of the transition fluctuations to elastic behavior. Thus

a primary thrust of the experiments will be to measure properties related to the phase transition and its underlying dynamics. A particular probe of these dynamics are acoustic techniques. Such techniques go directly at the problem of ultimate interest - the elastic property changes due to the transitions. To understand the mechanisms usually requires measurement of other material. For example to understand the elastic properties of ferroelectric crystals near the Curie temperature requires measurements of the dielectric susceptibility and the spontaneous polarization. The relaxation rates seen in attenuation are related to the damping of a highly anharmonic optical phonon.

A systematic study of high pressure-high temperature phase transitions is necessary so that many of the mechanisms affecting seismic velocities can be understood. Further, to the extent that the techniques can be extended to higher pressures and temperatures on geophysical materials, direct laboratory input to the interpretation of seismic data must be made.

### 3. Source Shapes

Anticipating the possibility of observation of large earthquakes with coupled seismographs we would like to study the distribution of waves produced by a non-point source. The method consists of constructing a Green's function for an isotropic elastic medium, approaching as close as possible the Green's function for an anisotropic medium. The non-point source can be assumed to be an extended point source or a sheet. One has to assume that the different sources that make up the point source all occur at the same time. If not, one has to

make a reasonable assumption about a time distribution. The solutions of such problems are only of importance in the near-zone (in the sense of antenna theory) since in the far-zone all possibility to see any structure may be lost due to the inhomogeneity of the earth's materials. The study would deal mainly with the observability of the "shape" of the non-point source.

## B. EXPERIMENTAL PHYSICS

The objectives here are: to characterize possible phase transitions processes, to test theories of phase transitions, properties and dynamics, to develop techniques of making ultrasonic and light scattering measurements at simultaneous high temperature and high pressure, and to measure the properties and phase transition phenomena at high temperature and pressure in materials of direct interest. More specifically it is proposed to develop techniques and apply them to study each chosen material with the following goals:

1. To locate the transitions (P, T, and possibly external field) in apparatus capable of dynamical experiments, acoustic, ultrasonic, optical hyper-sonic, and/or Raman scattering.
2. To characterize the transition thermodynamically by determining the transition pressure, temperature and field, measuring the lattice constants and lattice constant changes, measuring the specific heat and transition specific heat anomaly, measuring the dielectric and magnetic susceptibility changes.

3. To characterize the transition dynamics by detecting the type of instability, whether an optical vibration ("soft mode") or an elastic instability, and by measuring the space and time dependence of the transition "order parameter" fluctuations using acoustic and light scattering techniques.

The kind of measurement which can be carried out under such extreme pressure and temperature conditions is at present limited to relatively simple measurements such as electrical conductivity, volume changes and heat of fusion; nevertheless such measurements are fundamental in that phase changes can be observed and phase diagrams can be mapped out in hitherto uncharted regions for numerous materials. Much of the current high pressure literature has to do with this aspect.

Future possibilities would appear to lie in two general directions:

- a. Extension upward of the present limitations to pressure temperature, and working volume available for experimentation (which involves severe technological challenges).
- b. Advances in the degree of sophistication of high pressure experiments and the maximum pressure at which such sophisticated experiments can be performed.

As an example, the requirement that the sample area be accessible to a precision optical or ultrasonic probe imposes constraints of such severity that the current upper limits in pressure are drastically reduced from the aforementioned "unconditional" limit of 100 - 500 k bar. On the other hand, such

measurements are highly desirable (in conjunction with numerous other methods).

Recent advances in optical techniques in light scattering using lasers offer powerful tools for characterizing the crystal structure, molecular motions and phase transition dynamics of materials. These highly developed tools have been adding greatly to our knowledge of crystal and liquid phase transitions over a broad temperature range (2 to 1000°K) but all at relatively low pressures.

These optical techniques which look directly at molecular dynamic states can be adapted to high pressure. Much work in the past has gone into development of suitable windows for optical studies of materials at high pressure. We can use this technology together with the new tools in vibrational spectroscopy to study the high pressure phases of materials.

The acoustic methods are already highly developed but much work remains in using them to study phase transitions and to reach high pressure and high temperature while making measurements. The acoustic measurements complement the light scattering measurements of elastic constants by covering a broader frequency range and particularly the low frequency range. They have the further advantage of being usable for opaque materials such as metals, highly colored crystals, polycrystalline materials, etc.

#### 1. Description of the Techniques

##### Inelastic light scattering: Raman and Brillouin Scattering -

Inelastic light scattering spectroscopy consists of illuminating the sample in a chosen direction with a collimated monochromatic beam and determining

the spectrum of the light scattered out of the beam at a chosen scattering angle. In general a small fraction of the incident light is scattered with frequency shifts characteristic of the internal states of the material changed during the scattering.

If the light scatters off of an optical branch phonon in a crystal or an internal molecular vibration of a gas or liquid molecule then one sees a spectral component in the scattered light shifted by the phonon or vibration frequency. The spectrum for such events is called a Raman spectrum and generally lies in the 10 to 2000  $\text{cm}^{-1}$  range of frequency shifts. Resolutions of 1  $\text{cm}^{-1}$  are routine and by using lasers the directions and polarizations give anisotropic selection rules which allow precise mode identification. Raman scattering applied to solid-solid transitions shows the temperature dependence of the optic mode instability onset, classifies modes by polarization selection rules so that symmetry changes can be monitored by selection rule changes, and local symmetry by the splitting of internal molecular vibration frequencies. Applied to crystal-amorphous and amorphous solid-liquid transitions one can determine the density of vibrational states, and the correlation range of vibrations. If the light scatters off of an acoustical phonon then one finds a set of components in the scattered light spectrum called the Brillouin spectrum with components shifted by

$$\Delta\nu = \nu_o \frac{v}{c} \sin \theta/2$$

with  $v$  the acoustic velocity,  $\nu_o$  the incident light frequency,  $c$  the velocity of light in the medium and  $\theta$  the scattering angle. This shift can be thought of as

a Doppler shift due to the reflection of the light from the traveling acoustic wave. These frequency shifts for  $90^\circ$  scattering of visible light are from 0.4 to 50 Ghz. Thus such spectral components reveal properties of hypersonic acoustic modes.

Brillouin scattering basically gives another way to determine elastic constants but with advantages that it samples the local (small volume) thermal strain fluctuations in equilibrium, it senses the longitudinal and shear modes, and it allows one to study the velocity and attenuation anisotropies by merely turning the crystal with respect to the incident and scattered beams. The frequency range covered by the Brillouin spectrometer allows one to see very low frequency parts of the Raman spectrum. This is particularly interesting when the transition occurs because of the interaction of acoustic and optic phonon modes. The line-width of the Brillouin components can be used to determine the attenuation of the mode. This becomes measurable only in cases where the attenuation is extremely large as often occurs near transitions. In ultrasonics the high attenuation often limits how close to the transition one can study the acoustic modes. The scattering techniques have special advantages for phase transition studies. The advantages are that small (less than a cubic millimeter) volumes can be studied (giving small temperature and pressure gradients) with high precision, that long range and short range order motions can be seen and that the frequency range extends down to very low material frequencies (less than  $1 \text{ cm}^{-1}$ ). These advantages can all be realized in the proposed extension to high pressure phase transition studies.

## 2. Acoustics: Ultrasonic and Resonance

Pulsed ultrasonics consists of sending a short pulse of high frequency sound across a sample and detecting the echoes from a parallel opposite sample face. The echo spacing gives the travel time and hence the velocity while the decay of the echo heights gives the attenuation. Good direction and mode selection is possible and measurements can be made over a frequency range of 5 to 500 MHz quite conveniently.

We believe that many interesting phase transition mechanisms will exhibit some slow fluctuations which couple to acoustic modes. To detect these requires low frequency measurements say from 100 kHz to 1 MHz. These measurements are best done using resonance techniques. In these measurements the applied frequency is varied and the frequencies of resonant mechanical response are measured together with the frequency width of the response. With the sample dimensions known the resonance frequencies are used to calculate the elastic constants. The resonance widths are used to determine the attenuation expressed as  $Q^{-1}$ , the fractional loss per cycle.

A summary of known elastic constant data on some ten minerals (oxide and silicate compounds) relevant to geophysics has recently been given by Anderson (Reference 11). The minerals represented in this review include corundum ( $\alpha$ - $Al_2O_3$ ), periclase (MgO), a spinel ( $MgO \cdot 2.6Al_2O_3$ ), forsterite ( $Mg_2SiO_3$ ), a garnet (almandite-pyrope variety), hematite ( $\alpha$ - $Fe_2O_3$ ),  $\alpha$ -quartz ( $\alpha$ - $SiO_2$ ) and lime (CaO). These materials are representative of the Earth's crust and mantle,

the latter in particular being largely composed of compounds related to quartz and periclase. This data consists largely of laboratory-measured sound velocities and derived elastic moduli and their pressure and temperature derivatives, and the anharmonic Gruneisen parameters  $\gamma$  and  $\delta$  which relate the isothermal elastic moduli (relevant to equations of state) and the measured adiabatic moduli. It is largely on data such as the above that our present knowledge of the internal structure of the Earth rests, because without it no meaningful analysis of the propagation of seismic disturbances could be made.

Elastic properties, which may be determined by acoustic wave velocity measurements, provide information primarily on compositions and density. The study of acoustic velocity in the laboratory on geological specimens at elevated temperatures and pressures has the potential of improving the diagnostic power of seismic body and surface waves in determining composition and density in the crust and mantle of the earth. Acoustic wave attenuation studies in the laboratory illuminate the possible microscopic causes of seismic wave absorption. Thus far, much of the geophysical literature on seismic wave attenuation confines itself to macroscopic absorption mechanisms. To make laboratory studies relevant to geophysical phenomena as seen in seismic attenuation, the studies of microscopic attenuation mechanisms must be extended to high temperatures and pressures. Loss of energy from an elastic wave in a medium as complex as the earth's mantle could arise from several sources. One might mention scattering from inhomogeneities comparable with the wavelength (which is not a true energy

loss but a diversion of energy from the main direction of flow), hysteresis (due to irreversible changes caused by stress), viscosity, and any one of a large number of relaxation effects (reversible changes tending to relieve stress) which are all possible contributors. Fortunately, the frequency range of many such effects is incompatible with the range encountered in seismic investigations, and, according to a recent review (Reference 12), the most likely causes of loss of seismic energy are partial melting, grain-boundary relaxation, and a poorly understood mechanism called "high temperature, internal friction background."

Of particular interest to current geodynamical theories is the relaxation mechanism which may be present in materials undergoing phase transitions. Since many phase changes themselves are associated with a definite value of the ambient pressure, fluctuations of this pressure due to an elastic wave will tend to induce a reaction from one phase to the other which reduces the elastic stress and causes a relaxation effect, leading to attenuation. An acoustic wave passing across a phase boundary will suffer a sharp loss in energy, and the frequency range of this relaxation effect is in the right range to account for the attenuation of seismic waves. These ideas have been given experimental support by controlled experiments in suitably chosen model systems. In particular, Spetzler and Anderson (Reference 13) have reported discontinuities in the velocity and attenuation of sound in the System  $\text{H}_2\text{O}.\text{NaCl}$  in the regime of partial melting.

Attenuation mechanisms which are regarded as important in seismic absorption wave include dislocation mechanisms, intergranular thermoelastic

relaxation, and atomic diffusion. Therefore, the acoustic study of such mechanisms in the laboratory, on carefully characterized specimens and under controlled conditions of temperature and pressure, increases the power of natural and artificial seismic wave disturbances as diagnostic tools, and at the same time, gives direct insights into mechanisms which have significance for dynamical processes in the crust and mantle.

### 3. State of the Art: Phase Transitions

To give some context to the measurements possible with acoustic and light scattering methods we will briefly review the recent progress in the physics of phase transitions as viewed from the experimental point of view. Strong new inputs to the fields of statistical mechanics and lattice dynamics from the close interaction between theory and experiment, has resulted in progress and increased interest in the problems of phase transitions during the past six years dating from the 1965 Critical Point Conference at the National Bureau of Standards (Reference 14). A theme in the new work has been to understand the cause and effects of the divergent fluctuations of thermodynamic variables at second order phase transitions. The more difficult first order transitions have received much less attention, but experiments done very close to the transition points have shown that many transitions having large fluctuation effects finally do exhibit first order transition steps in thermodynamic derivative properties and do show hysteresis. Thus much of the conceptual progress can be applied to understanding first order transitions with large fluctuations. In particular there is hope of using these new ideas in studying further aspects of the melting transitions.

In the current usage of the theory all divergent fluctuations are called critical fluctuations and the second order transitions associated with them are called critical points. Fundamentally the problem remains often unsolved in terms of theoretical calculations, but a heuristic theory, using exponents to describe the nonanalytic behavior near the critical point with relations between exponents coming from thermodynamic inequalities, has been very useful in relating various transitions (liquid-vapor, magnetic, order-disorder alloys, etc.). These ideas have been also proven to be useful for comparison with theoretical attempts to determine limiting behavior numerically.. A review of the current position is given by Stanley (Reference 15).

Experiments, in particular light scattering experiments, have resulted in a further extension of the theory namely the description of transport coefficients near the critical point (viscosity, thermal conductivity, dielectric relaxation, etc.) in order to describe and understand the dynamics of the critical fluctuations. Here again the best of the current suggestions have amounted to an extension of the static "scaling" exponent relations to dynamics mainly with the view of relating all the observed temperature dependences to that of the correlation range of the fluctuations. There have been recent indications that such theories may be rather oversimplified however.

The light scattering experiments testing the exponent theories were mainly done on the liquid-vapor critical point. From the temperature dependence of the intensity of scattering the divergence of the fluctuations could be established with

good precision and from the angular dependence of the intensity the correlation range temperature dependence was found. These experiments were helped materially by the availability of laser sources and improved sensing and control electronics of the temperature baths. The measurements of the linewidth of the quasi-elastic (Rayleigh) scattering depended essentially on the collimation and intensity of the continuous gas laser beams. These measurements gave for the first time an opportunity to study the dynamics of the fluctuations; the linewidth measured the decay rate of selected Fourier components of the critical density fluctuations. The linewidths go to zero as the critical point is approached corresponding to the slowing down of the large fluctuations. The high precision linewidth data showed an unexpected exponential behavior. Since the linewidth was proportional to the thermal diffusivity this provided strong evidence for the divergence of the thermal conductivity at the critical point. A discussion of the method and review of the results can be found in Swinney & Cummins (Reference 16).

Light scattering measurements of intensity and linewidth have also been applied to critical mixtures. The scaling theories have worked well here and the measurements which describe the concentration fluctuations and their rate of decay, show strong similarity to other critical points. These mixture problems may be very significant for the molten regions of geophysical interest. The strong changes in low frequency sound velocity and large attenuation for sound frequencies up to several hundred MHz could have a large seismic influence.

It is of interest that all critical points cause large peaks in acoustic attenuation. The latest experiments using acoustics and Brillouin light scattering (scattering off the acoustic modes of a material) have obtained a better foundation due to the calculations of Kawasaki (Reference 17), who showed how to relate the space-time dependence of the critical fluctuations to the observed distributed velocity and loss dispersion. Attempts have been made to apply this theory to critical mixtures but have not been very successful in predicting the magnitude of the dispersion. In particular the thermodynamics of predicting the low frequency sound velocity has not been successfully carried through. The velocity dispersion which does occur should take place at very low frequency for mixtures. It appears that more experiments in this field are needed.

During the same period there has been an active development in the ideas of the lattice dynamics of second order solid-solid phase transitions. Here the leading idea is to understand the microscopic nature of the structure change and the dynamics of the critical fluctuations in one or a small number of vibrational normal coordinates as due to a "soft mode." A soft mode is a particular optical vibration of the structure which is renormalized by phonon interactions and this renormalization becomes unstable. Consequently its frequency goes to zero and the lattice lowers the symmetry of its unit cell by an internal distortion corresponding to the displacements of the soft mode at the temperature and pressure of the phase transition. The ideas was pioneered by Cochran (Reference 18), and first confirmed by Cowley (Reference 19) in the perovskite  $\text{SrTiO}_3$  using inelastic

neutron scattering. This idea was further pursued by laser Raman scattering (scattering off the optical branches of the lattice vibrations) because of its increased energy resolution and mode selection by polarization.

Of particular interest for exploring new transitions is the ability of using selection rules predicted by group theory and the crystal point group describing the polarizations of the light scattered by different modes. This leads to very interesting temperature dependences of modes which are not soft modes but which are forbidden on one of the phases and thus show by their intensity the temperature dependence of the continuous changes in structure.

This procedure can be reversed in order to yield details of the symmetries of the phase on each side of a transition by counting the allowed modes of each polarization type in spectra taken in the two phases. With the additional information from the splitting caused by lowered site symmetry it may be possible to assign a unique structure. This kind of detail is usually not available in the corresponding x-ray diffraction data since it is lost in the thermal diffuse background around the superlattice spots.

Finally a third class of experiments studying the effects of phase transitions on elastic constants which goes back to the work on ferroelectrics by Mason (Reference 20) and others and Russian studies of Rochelle salt (Reference 21), was revived and extended by the new experiments using Brillouin scattering on crystals at the phase transition (References 22 and 23). Here one looked for the coupling of the soft mode (critical fluctuations) to change the sound velocity and

cause acoustic losses. Using the suggestion of relaxation by fluctuations made by Landau and Khalatnikov (Reference 24), the relaxation times found in the experiments were taken as a measure of the decay of the critical fluctuations and hence their temperature dependence could be tracked with higher precision and closer to the transition than was possible with the Raman experiments. The significance of large losses in the coupled mode problem has recently been realized so that it is now possible to relate the linewidths of soft-modes to the acoustic relaxation found with Brillouin scattering. Of particular significance here is the simple use that has been made of point group symmetries to arrive at reliable predictions concerning questions as to which modes can be soft, which modes can couple to the soft mode and particularly which acoustics modes (longitudinal or two kinds of shear and their direction) can be changed by the soft mode fluctuations. This includes the possibility of being able to predict whether the velocity will simply undergo a step (plus large losses) or will show a strong decrease to zero, leading to a homogenous deformation instability at the transition. The theories for the acoustic mode-behavior near the critical solid-solid transitions apply to ultrasonic, sonic or acoustic measurements as well as to the Brillouin scattering experiments. The only difference being that the Brillouin scattering are always at higher frequencies. Thus there exists a large body of newly refined work on the nature of sound velocity variations and acoustic losses near phase transitions which we here propose to apply to geophysical transitions.

The materials of interest to geophysics either as model systems or directly which have been studied so far during the recent years are:

(1) The alpha-beta phase transition in quartz; (References 25 and 26). An unstable optical mode was found but it did not strongly effect the elastic constants (only a step) while hysteresis was apparent in both the Raman and Brillouin data. The opalescence of the phase boundary was established to be due to static phase boundaries and not due to critical fluctuations. The experimental work is an example of high precision light scattering at elevated temperatures.

(2) The ferroelectric transition in KDP; (References 23 and 27). Here the soft mode was seen as overdamped and the zero in acoustic velocity was followed into 10 millidegrees of the transition for the  $C_{66}$  shear mode. This is an example where the symmetry allows direct coupling of the soft mode and an acoustic mode, giving very strong effect on the velocity. It drops to zero at the transition.

(3) The ferroelectric transition in TGS; (References 22 and 28). Here the relaxation due to fluctuations was identified and the relaxation time measured including its temperature dependence with confirmation in detail of the predictions of allowed couplings to acoustic modes. Here the largest change in velocity was 10% for a shear mode. The acoustic attenuation was very large.

(4) Perovskites, cubic to tetragonal transition; (Reference 29). The perovskite lattice is particularly prone to instabilities. These have been studied with neutrons, Raman scattering and Brillouin scattering as well as with ultrasonics. The soft modes have been well characterized and the allowed coupling

to sound modes predicted. One expects steps in elastic constants at the transition and large acoustic relaxation near the transition. The relaxation time has not been very well determined. The transition is of interest because several geological materials are believed to have a high pressure transition to the perovskite structure. So far no spectroscopic pressure measurements have been made at high pressure on the above transitions.

(5) Liquid mixtures; (Reference 17). Here there is need to learn how to make reliable estimates of the magnitude of the coupling of the concentration fluctuations and the low frequency velocity and attenuation. This is one of the most general possible loss mechanisms. It is unfortunate that it remains so poorly understood. No work has been done on the nature of such transitions at high temperature and pressure.

Finally the whole class of melting transitions has not benefited from recent ideas. It would be of great interest to see how much could be learned about the nature of the instabilities leading to melting and if the fluctuations due to the instabilities cause large intrinsic acoustic losses. Since there have been many suggestions concerning the connection of melting or partial melting to the density and velocity profile below the crust it seems appropriate to learn as much as possible about the phenomena in the laboratory. We propose an attack on these problems below.

#### 4. Types of Transitions

Transitions can be broadly grouped into first order and second order transitions. The second order transitions have received the most attenuation in theory

and experiment. They exhibit no discontinuities in thermodynamic variables but have divergent fluctuations in one or more variables. Understanding and relating the divergences has been the theme of the work. The problem of interest here is that the diverging fluctuations invariably cause acoustic attenuation and velocity changes.

Examples of such transitions are: liquid-vapor critical points, liquid mixture critical points, ferroelectric Curie points, ferromagnetic Curie points, internal molecular orientation ordering as in  $\text{NH}_4\text{Cl}$ , etc. The most interesting sub-class of these transitions are those which allow a direct, linear coupling of the sound strains to the critical variable. This always results in an elastic instability with strong attenuation and velocity changes. An example is the solid-solid ferroelectric transition in potassium dihydrogen phosphate.

The first order transitions are much more varied. They are harder to study theoretically and experimentally. They exhibit discontinuities in one or more thermodynamic variables and usually much smaller fluctuation phenomena. A classic example is the solid-liquid transition, melting-freezing. At low pressures there are several examples which should be studied; melting of simple molecular crystals, plastic crystal transitions in which some partial molecular ordering occurs, and the glass transitions in the material never crystallizes but remains in a disordered state. There have been many suggestions that one should find a shear mode whose velocity becomes very low to trigger the melting. This idea is too simple but has not seriously been challenged by experiments.

At high pressures possible new kinds of melting occur. High pressure melting has been reported in alkali metals and in  $\text{KNO}_3$  and  $\text{KNO}_2$ .

Liquid-vapor systems away from the critical point have first order transitions. Here the acoustic modes are influenced by the nearby fluctuation instability at the spinodal.

Liquid mixtures offer many examples of liquid-liquid transitions. These may be very important because of their influence on partial melting transitions of mixed materials. The influence of concentration fluctuations is not well understood at present but has received increased attention due to the critical point studies and so is ripe for progress.

A basic and essential part of first order transition dynamics involves the ideas of condensation. The basic idea of condensation rates has always been based on the presence of small particles: if they are present the rate is finite, if not the rate is zero. This in turn is based on the minimum radius of nucleation. Droplets have a volume energy and a surface density and a simple estimate of both lead to a condition which shows that beyond a certain radius the energy is diminished when the radius is increased. It is generally assumed that the presence of small particles will establish the necessary minimum radius. However very little is quantitatively known. Is it possible to confirm the fact that particles too small will indeed be without help in triggering condensation? Is the size of the particle the only relevant parameter? What is more precisely the role of the particle-gas interaction and can one apply the theory of surface

tension to dimensions this small? Experiments are proposed to study this phenomenon.

#### 5. Samples Proposed for Study

As an experimental philosophy it is proposed that the search for suitable "model" crystals be made which show characteristic solid-solid and solid-liquid phase transitions at accessible temperatures and pressures. These will serve as baseline studies for interpretation of the later and more difficult studies at high temperature and pressure. On a longer time scale work should begin on the development of pressure temperature vessels with suitable experimental parts for pursuing studies of the phase transitions in mantle materials, silicates and magnetic iron compounds. Experiments are proposed which cover as wide a range of temperature and pressure as possible consistent with precise use of light scattering and acoustics on the following samples:

1. Potassium dihydrogen phosphate and its isomorphs: electric ordering with elastic instability.
2. Cubic perovskite materials,  $\text{SrTiO}_3$ ,  $\text{RbMnF}_3$ , etc.: orientational ordering, magnetic ordering, elastic instability.
3. Molecular crystals:  $\text{-Xe}$ , methane, benzene, etc.: melting dynamics.
4. Fused salts: glass transition melting.
5. Magnetic iron oxides:  $\text{Fe}_2\text{O}_3$ , etc.
6.  $\text{KNO}_3$ : high pressure melting.
7. Quartz: follow the transition dynamics to high pressure of the alpha-beta transition.

8. MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and CaO mixtured compounds: search for and characterize transitions.

## 6. Equipment for the Program

Initial commercial equipment

1. Single frequency argon laser
2. Double grating monochromator Raman apparatus
3. Fabry-Perot Brillouin spectrometer with electric drive and multiscaling capability.
4. Matec precision ultrasonic velocity and attenuation recorder.
5. High pressure diamond anvil optical cell.
6. Precision potentiometer for temperature measurements.

Apparatus to be designed and built.

1. 10 k bar hydrostatic cell with liquid transfer medium for optical measurements with internal and external thermostatted jackets.
2. Same as (1) but for ultrasonic and or resonance measurements.
3. Drickhamer type very high pressure optical cell for scattering.
4. Cubic anvil high pressure ultrasonic cell with anvils used as buffer rode between external transducers and the sample.

## 7. Initial Experiments

The initial steps in the light scattering program are two classes. The first will be survey experiments using Raman scattering and the very simple to use diamond anvil cell to explore the pressure dependence of known phase transitions and provide some microscopic mode picture of the transition. We will

emphasize the low frequency part of the spectrum for P, T points close to the transition. This is where the transition dynamics will appear.

The second class of experiments will involve Raman and Brillouin scattering and their relation at several mode transitions initially at low pressure: ferroelectric crystal transitions, molecular crystal melting, glass transition melting, and liquid mixture critical points. These three types of transitions will then be explored for pressure dependence in the low pressure, hydrostatic pressure cell in order to understand the pressure-temperature dependence of the dynamics. A fifth member of the class will be experiments on the condensation dynamics in metastable regions. This work will be done on liquid-vapor systems and on the molecular crystal freezing.

As experience with pressure apparatus and first order transitions dynamics increases we will be ready to move to materials of more direct geophysical interest in measurements of transition dynamics at very high pressures.

As an example of the experimental study of a phase transition the following description is included of the steps in studying the elastic instability in potassium dihydrogen phosphate. Potassium dihydrogen phosphate (KDP) and its chemical and deuterated isomorphs exhibit phase transitions with the special features of: (1) strongly coupled lattice and hydrogen bond motions and (2) elastic shear instability at the transition. This second property is of special interest as model behavior for solid-solid phase transitions with elastic instability (i.e., a strong decrease to zero of the shear mode velocity at the transition) which might give rise to the velocity dips in the lithosphere seen in the seismic measurements.

In the last three years three important advances have been made: (1) Raman scattering was used by Kaminov and Damen to find the overdamped "soft mode" optical lattice vibration in KDP, (2) Brillouin scattering show that the xy shear mode which becomes unstable can be studied far enough into the transition to determine the relaxation rate of the critical fluctuations at the transition, (3) ultrasonic velocity and attenuation measurements in KDP and deuterated KDP shows the strong effect of hydrogen ion mass on the transition dynamics and the relation between attenuation losses and soft made damping.

The following set of experiments are proposed:

- (1) To measure the Raman and Brillouin light scattering spectra of deuterated KDP to establish the unstable optical and shear mode dynamics near the transition.
- (2) To measure the Raman and Brillouin light scattering spectra in the isomorphic crystals potassium dihydrogen arsenate and its deuterated form to determine the mode dynamics at the transition and by comparison with the results in KDP to relate the critical mode dynamics to the mass and force constants of the phosphate-arsenate ion.
- (3) To measure the Raman and Brillouin light scattering spectra in the isomorphic crystal ammonium dihydrogen phosphate and its deuterated form. These crystals become anti-ferroelectrically ordered at the transition and hence lack the long range electric forces which occur in KDP. This is expected to strongly change the mode dynamics.

- (4) To begin the first light scattering measurements under pressure on KDP and its isomorphs. Recent work has shown that the transition temperature is strongly decreased by pressures between 0 and 40 kbars but no work has been done to determine the change in the mode dynamics with pressure. The initial work proposed here will be to determine the changes in the Raman soft mode spectrum near transitions at elevated pressure using a diamond anvil optical cell.

In the study of solid-solid phase transitions a powerful complement to the use of light scattering as an investigative probe is the acoustic technique. While Raman and Brillouin scattering are extremely informative at high frequencies for studying the optical and acoustic modes and their coupling, ultrasonic measurements are essential if we are to continue to follow the phase transition dynamics to low frequencies close to the transition point.

Since the elastic instability is ultimately limited to low frequency long wavelength modes, it is essential to be able to extend observation of the transition to lower frequencies. Since the "soft" optical mode(s) is often strongly coupled to shear elastic mode(s), acoustic shear waves at frequencies extending downward from 100 MHz to the KHz range and below are needed to the study of solid-solid phase transitions.

It is valuable for gaining insight into geologically important solid-solid phase transitions to carefully choose model systems for experimental investigation in the laboratory in which the presence of an elastic instability is associated with solid-solid phase transitions.

It is proposed that solid-solid phase transitions in isomorphs of KDP (potassium dihydrogen phosphate) be studied through the shear wave velocity and attenuation measurements very close to the phase transition, over a wide range of acoustic shear wave frequencies. From the attenuation as a function of temperature near  $T_c$ , and the velocity of the shear waves near  $T_c$  (for a range of frequencies) the coupling of the optical and elastic modes near the transition and the relaxation times for the solid-solid phase transitions will be studied—and in this way give information on the nature of the instabilities associated with the model solid-solid phase transitions.

These phase transition studies must then be examined at successively higher pressures—initially, pressures to 10 kilobars, using available techniques. It is speculated that for isomorphs such as ADP (ammonium dihydrogen phosphate) high ambient pressure may actually improve the likelihood of making the measurements on large crystalline specimens, since fracture is readily experienced as one runs through the transition at atmospheric pressure.

Further, it is proposed that the above-mentioned effort then be extended to poly-crystalline specimens, studied at low shear-wave frequencies. Systems of geophysical interest rarely have macrocrystalline structure. For many purposes the low frequency (i.e., long wavelength) shear waves will continue to give information on the solid-solid phase transition despite presence of macroscopic inhomogeneities. Thus, for example, for  $D \gg \lambda \gg d$ , where  $\lambda$  is the shear wavelength and  $D$  and  $d$  are, respectively the specimen and crystalline dimensions, the

data should be reasonably free of complications attributable to grain-boundary scattering effects. At the same time, it should continue to be possible, despite the poly-crystalline character of the specimens, to study dispersion associated with the instability-related mode coupling and the relaxation times, for a phase transition, very close to  $T_c$ .

## C. THEORETICAL PHYSICS

### 1. High Pressure Melting

Under normal pressures the melting temperature of a crystal increases as the pressure increases. This means that the higher is the temperature of a liquid the larger the pressure of solidification becomes. But recently, it has been found that many substances show a maximum temperature of solidification. This means that as the pressure is increased the solidification temperature increases for a while, reaching a maximum, and then decreases as the pressure is further increased. This in turn means that at a fixed temperature when a liquid is compressed it becomes a solid at a certain pressure but if the pressure is further increased, the solid again becomes a liquid. This phenomenon is called the high pressure melting. This high pressure melting is a rather prevailing phenomenon observed in many different substances. As mentioned above, examples are barium, tellurium, europium, antimony, carbon, Rb, Cs, the intermetallic compounds  $\text{Bi}_2\text{Ti}_3$ ,  $\text{Sb}_2\text{Te}_3$  and  $\text{PbTe}$ , and inorganic salts  $\text{KNO}_3$  and  $\text{KNO}_2$ . The high pressure melting has a very important implication in the geo-dynamical instabilities and an anomalous feature of seismic wave propa-

gation. There are many indications that there is a zone of partial melting in the mantle, and this is in turn related with the discontinuity of the density.

To understand the mechanism of high pressure melting is, therefore, one of the most important topics of solid state physics approach to geodynamics research.

Improvement in the theory of high pressure melting can be made as follows:

(1) Order-Disorder Theory of Melting (Weiss Approximation)—According to present analysis, the Yoshida-Okamoto model does not explain the high pressure melting as soon as the approximation is improved to include the effect of short range order. It is therefore necessary to find a condition on the interaction potential which gives the high pressure melting regardless of the nature of approximation. It is suggested that the combination of exponential potentials, one is repulsive and the other is attractive, and a short range inverse power repulsive potential would be a physically most plausible potential which would explain the high pressure melting and hence the equation of state over wide range of temperature and pressure.

(2) Order-Disorder Theory of Melting, Two-Body Approximation—it is generally known that the one body Lennard-Jones-Devonshire (L-J-D) approximation gives values of physical quantities which are some 20% off the accurate values although qualitatively correct. To predict the melting curve, the relation between the melting temperature and pressure, more accurately and calculate other equilibrium properties, such as the latent heat of melting, one has to

extend the theory to include the two-body and three-body correlations. Investigation along this line will be pursued.

(3) Theory of Melting of Molecular Crystals, Weiss Approximation—Before attempting the application of Yoshida-Okamoto type theory of high pressure melting to mineral crystals which are combinations of  $\text{SiO}_2$  and  $\text{MgO}$ , the extension of L-J-D type theory of melting to molecular crystals must be achieved. For instance, the mechanism of melting of ice is very different from that of monatomic substances. If the molecules in the crystal in the vicinity of melting points are rotating very rapidly, then the effective potential between molecules may be approximated by a spherical interaction and hence the L-J-D type theory is applicable. If, however, molecules executed hindered rotations in the solid phase and molecules undergo free rotation in the liquid phase then in the process of melting two disordering effects take place simultaneously, i.e., the rotational disorder and the configurational disorder. Formulation of the theory of melting of this nature is of prime importance. This must be first achieved in the Weiss approximation in order to understand mechanism of melting qualitatively.

(4) Theory of Melting of Molecular Crystals, Two-Body Approximation—After establishing qualitative understanding of the mechanism of melting of molecular crystals in the Weiss approximation now the investigation of the effect of short range correlation is required. There are spacial correlations just like in monatomic crystals, and the orientational correlation due to the molecular structure of the crystal, but also there will be a cross-correlation between the

spacial distribution and the orientational distribution. Because of this correlation the simultaneous onset of spacial and orientational orderings would be possible and this effect would have a very important implication in the dynamics of phase transformations, especially in the mechanism of sound wave attenuation in molecular crystals in the neighborhood of the melting point. This situation is quite analogous to that in sound attenuation in the diatomic gas where the energy transfers from the translational degree of freedom to those of molecular rotation and vibration.

(5) Theory of Melting of Covalent Crystals— $\text{SiO}_2$  and  $\text{MgO}$  crystals are not the aggregate of molecules by means of weak van der Waals attractive interactions. These crystals have a feature of molecular crystals on the one hand because of their multi-atomic structure but the mechanism of binding is very different from that in the molecular crystals on the other hand. It is, therefore, necessary to find effective interactions which can be used in the statistical mechanics formulation of phase transformations in such crystals.

## 2. Lattice Gas Theory

It is proposed to restudy the general properties of the transition point(s) in the lattice gas. Recent work has shown that scaling factors are not as universal as they were once thought to be. Different values were found when the interaction was not restricted to nearest neighbors only. Since this is of direct interest to the problems described above we propose to study three dimensional lattice models with interactions that are beyond nearest neighbors or anisotropic or both.

These studies will be undertaken by (a) methods using truncated hierarchies;  
(b) series in low or high temperatures with exact coefficients.

This study will be combined with the evaluation of dynamic theories, using the exact temperature series method. The recent modifications of this method to enhance nucleation centers by various assumptions about the energy of such "droplets" may prove valuable in the theory of solid-solid or polymorphic phase transitions.

Further studies with dynamic theories will be made by using the description Kawasaki gives of the soft mode theories. It must be possible after long and careful studies to predict the occurrence of this phenomenon in specific substances.

### 3. Theory of Solid-Solid Phase Transition

Recent work shows the importance of ionicity versus convalency in phase transitions. Earlier work was simply based on ionic radii. These two ideas are not mutually exclusive; one needs a unified theory using both. We propose to do this using the techniques of the molecular field model, or similar and better techniques, to describe the solid-solid phase transitions by means of spin flops. In such a spin-analogy model the pressure plays the role of the magnetic field.

### 4. Solid-Liquid Phase Transitions

The solid-liquid phase transition as a function of pressure needs a new theory. The Lindeman expression though reasonable from the theoretical point

of view is not followed by a number of compounds. It is clear that the basis of the theory is wrong and we want to study the heuristic explanation given recently in order to give it a theoretical basis.

#### 5. Theory of Liquids Under High Pressure

It has been shown that the major features of liquids can be described by the hard core model. Deviations between the hard core model are:

1. Almost unobservable in the case of metals,
2. Small in the case of rare gas atoms, and
3. Different in case of non-spherical molecules, such as water.

All these observations are true under normal pressures. We speculate that under high pressure category #2 will first go over into category #1. It is planned to study case #1 under very high pressure, since little is known in this region. This would be done by studying the solid metal which seems to have very similar properties to the liquids. The theory for metals under high pressure will consist normally of the overlap of core wave functions which at normal pressure were well separated. Even more difficult, is the study of nonspherical molecules.

#### 6. Kinetics of Phase Transformations

This is the branch of statistical mechanics which has not been developed extensively until recently. However, the development of theoretical treatments in the past few years is very remarkable and the bulk of references is accumulating rapidly. Recently more exhaustive studies employing the scaling law

ideas, have noted that dynamical scaling partially holds. As was discussed earlier the law of corresponding states (sometimes called the scaling law, which is more common in recent years) holds for the equation of states for substances in which atoms interact with a common law of forces. The same is true even for dynamical properties especially near the temperature of phase transformations. However, the dynamical scaling is not a direct consequence of straight forward application of statistical mechanics, but rather is based on some phenomenological considerations. The key idea underlying the law is that there are a set of variables called the critical dynamical variables (CDV), such as the local density and local currents (mass current, energy current, electric current, etc.), and these variables satisfy a hierarchy of coupled equations. If the hierarchy is cut at some stage based on some intuitive arguments, then the coupled equations are terminated and closed for the set of critical dynamic variables. Solving those equations, which are usually integral equations, one finds some useful physical quantities such as the sound velocity, which is related to the imaginary part of and frequency dependent, specific heat; the diffusion constant; etc. Mathematical formulation of the scaling law is rather abstract, however; the result, like a thermodynamical theory, explains various relations among dynamical variables rather remarkably well. Since this kind of formulation does not start with the Hamiltonian it is most suitable even to discuss the dynamical properties of as complicated a system as geological mineral crystals. This kind of approach will be very promising for the coming

few years or even for much longer periods. Critical application of this approach to geodynamical phenomenon should be attempted.

There is another approach which is of entirely different nature. This is the traditional method of Hamiltonian quantum statistical mechanics. As was mentioned earlier, one starts with the Fourier transform of the time dependent correlation function. There are two methods of calculating the time dependent correlation function. One is the method of two-time Green's function, which has been proven to be very effective in the theory of ferromagnetic spin waves and in the theory of superconductivity. The second method is a direct application of many body perturbation theory and to calculate many terms of infinite series. This method too has been pursued very extensively in recent years and proven to be useful. In the second method again the use of computers is essential. We are now able to calculate time dependent dynamical properties in steadily increasing order of accuracy. The straightforward application of this technique, however, to geodynamics problems is not yet trivial.

## 7. Condensation

The purpose of this project is the study of metastable phase transitions: under cooling and superheating. What are the factors that determine the probability of obtaining such states if one starts from a point on the P.V.T. surface where P and T determine V uniquely? In the gas-liquid transition and in the transition associated with the mixing and demixing of two liquids we are interested in a specific study of the influence of impurities: their size, shape, surface forces, etc.

In the region of metastability the return to equilibrium can be described in two very different ways. One is the use of the free energy as a function of an order parameter in order to describe the metastable point as a secondary minimum. In this type of theory, widely used since Landau gave this picture for the case of ferro-electrics, the sample is treated as a homogeneous substance. The other type of theory is to consider nucleation centers and the buildup of the condensate around these centers. It seems that these two ideas are complementary and one should try to formulate a unified type of theory in order to be able to incorporate both aspects of the disappearance of the metastable state. It must be possible to have a more fundamental start using Green's functions in a way similar to what has been done in the theory of superconductivity of the second kind.

The second part of the program deals with liquid solid transitions. This will involve studies of computer simulated crystal growth. This type of work was started recently and looks very promising for the "detection" of the early stages of solidification. The work consists of a computer solution of the motion of a set of particles contained in a box with or without a prearranged condensate at a certain region in the box. By applying the equivalent of "lowering the temperature" one can increase the amount of solid. Ideally one should not use a prearranged solid, as this introduces the problem of recognition. It is desirable to attempt a new method: angular correlation over a few shells.

## 8. Theory of Magnetic Materials

Paleomagnetic research is important in connection with the polar wandering. A crucial fact should be pointed out that magnetite ( $\text{Fe}_3\text{O}_4$ ) undergoes a magnetization reversal as the temperature is lowered across the compensation and more complicated behaviors of magnetization, as a function of temperature, are seen in titanomagnetite and ilmenite-hematite. It is therefore necessary to know the accurate temperature dependence of magnetization in those crystals.

Magnetism is one of the most well developed areas of solid state physics both experimentally and theoretically and application of these techniques to rock magnetism should be most straightforward.

#### IV. CONCLUSION

We have discussed briefly, the various parts of Statistical and Solid State Physics which are of importance to Earth-Physics. It has long been observed that society is greatly benefited when scientific inquiry is stimulated and the various disciplines begin to converge on a common problem beneficial to all. Most exciting and fundamental have been the interactions among geology, geomagnetism, marine geomorphology, micropaleontology and tectonophysics to provide new insight into Earth Sciences. The task ahead is a formidable one since the microscopic analysis must be joined by a macroscopic analysis. Such a functional dependence of the various scientific disciplines upon a microscopic analysis as outlined in this report, is presented in Figure I.

After a great scientific theory has been developed, it takes many years to apply it to all of the relevant parts of nature. Newtonian Mechanics took 200 years to be completely applied to astronomical problems. Maxwell's theory has been a continuous source of successful application during the last hundred years. The development of Quantum Mechanics in 1925 was the same major breakthrough. It was immediately applied to simple atomic and molecular systems with great success but its applicability to more complicated systems such as crystals and liquids has taken longer. As always, there must coexist with such theory, suitable technology to exploit a given area of nature. In the opinion of those best qualified to know, the study of Earth physics has now reached such a crucial stage where the sophistication of theory and experiment have developed

sufficiently such that a major effort can be launched to understand the problem. The program will require the combined efforts of theoretical and experimental physicists, hydrodynamicists, rheologists, space scientists, etc. The payoff, however, is so enormous in terms of scientific, economic and social advance that the problem deserves a very high priority.

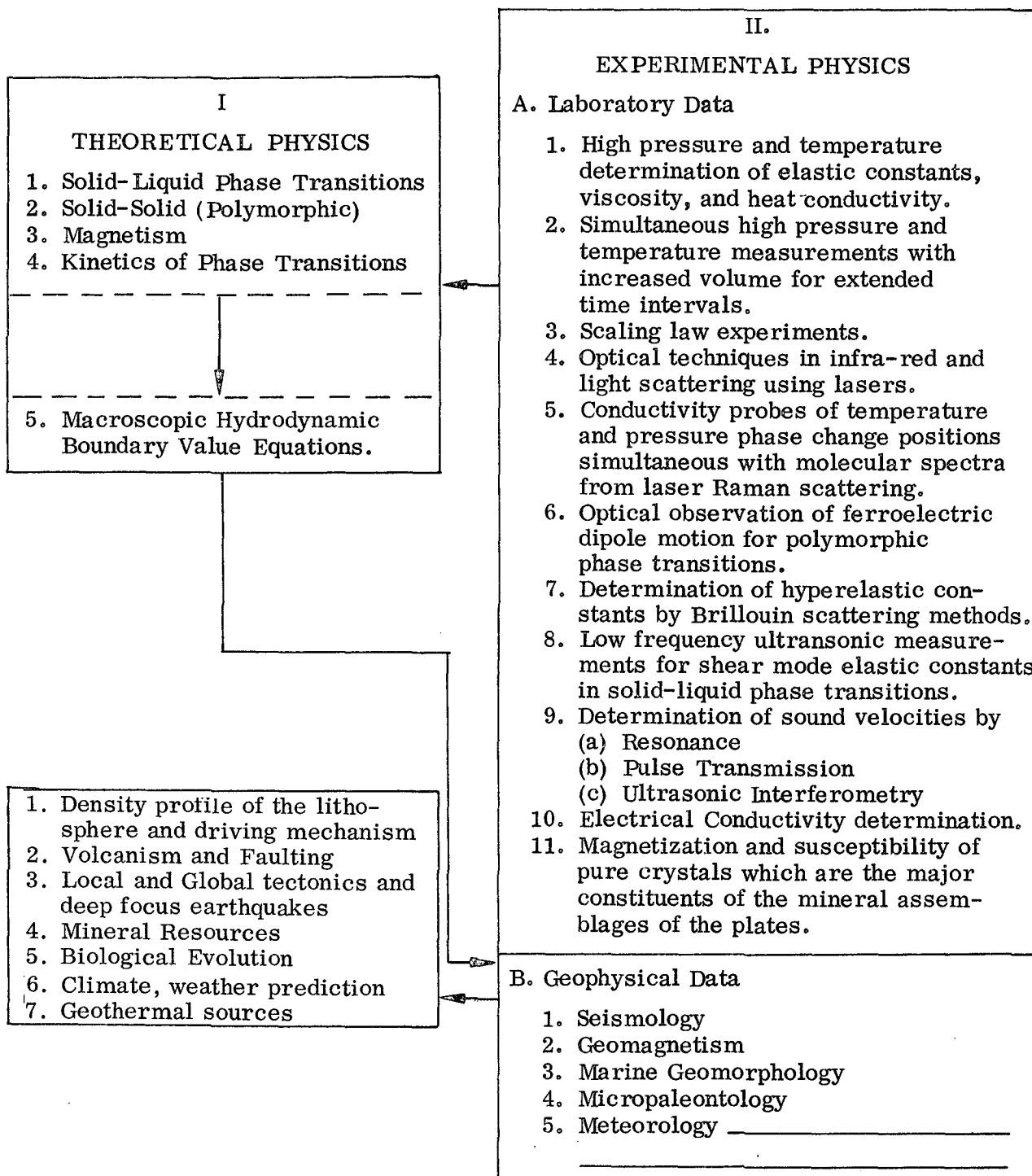


Figure 1. Earth-Physics and Phase Transition Program.

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